

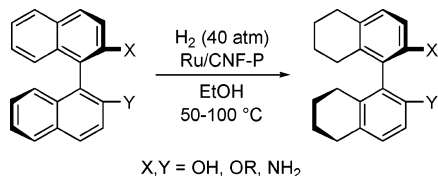
Highly Efficient Synthesis of Optically Pure 5,5',6,6',7,7',8,8'-Octahydro-1,1'-bi-2-naphthol and -naphthylamine Derivatives by Partial Hydrogenation of 1,1'-Binaphthyls with Carbon Nanofiber Supported Ruthenium Nanoparticles

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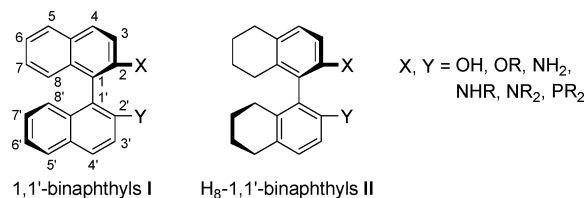
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Use of Ru/CNF-P, nanoruthenium particles dispersed on a nanocarbon fiber support, realizes highly efficient catalytic partial hydrogenation of 1,1'-bi-2-naphthol and -naphthylamine derivatives. The reactions proceed in high turnover numbers without racemization of the axial chirality, offering a practical procedure for the production of optically pure 5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyls in good to high yields.

Optically pure 1,1'-binaphthyls with C₂-symmetry such as 1,1'-bi-2-naphthol (BINOL), 2,2'-diamino-1,1'-binaphthyl (DABN), 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP), and their derivatives (**I**) have been widely used as chiral ligands for catalytic asymmetric syntheses.¹⁻³ It is also recognized that monoprotected BINOL derivatives such as 2-hydroxy-2'-methoxy-1,1'-binaphthyl (BINOL-Me) and 2-hydroxy-2'-(pivaloyl)-

oxy derivative (BINOL-Piv) are efficient chiral auxiliaries or precursors for the synthesis of non-C₂-symmetric 1,1'-binaphthyls.⁴ Chemical modification of naphthyl units in these chiral binaphthyls sometimes enhances the properties as chiral ligands.^{2,3} In particular, 5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyls (H₈-binaphthyls, **II**) have recently received considerable attention from organic chemists; they are more soluble and better electron-donors than the corresponding binaphthyls.⁵



In the complexes containing a ligated metal center at the 2,2'-positions, the H₈-binaphthyls show larger bite angles than the binaphthyls.^{6f,g} These properties sometimes provide higher asymmetric induction than the parent 1,1'-binaphthyls.^{5,6} As typical examples, H₈-binaphthyls are effective for alkylation of aldehydes,^{6a,b} hetero-Diels-Alder reaction of Danishefsky's diene,^{6c,d} and hydrogenation of alkenes.^{6e-g} Despite their potential as better chiral auxiliaries, synthetic procedures for H₈-binaphthyls are problematic. Although partial hydrogenation of 1,1'-binaphthyls with transition metal catalysts is a simple method for the synthesis of H₈-binaphthyls, the catalysts reported in literature showed poor activity and sometimes formation of an intermediary 5,6,7,8-tetrahydro-1,1'-binaphthyl (H₄-binaphthyls) as a byproduct.^{2a,7} Moreover, the reactions were often accompanied by racemization of the axial chirality.⁸ For example, catalytic hydrogenation of BINOL to H₈-BINOL over Raney-Ni/Al alloy, Ru/C,^{7d} or Pd/C^{7a,d} requires a high substrate/

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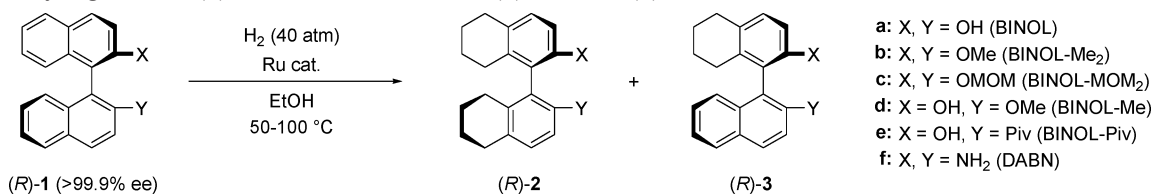
(8) Both BINOL and H₈-BINOL lose their optical rotations by heating in alcohols over 100 °C (~2%), and such partial racemization accelerates under acidic or basic conditions (~56%). *Encyclopedia of Reagents for Organic Synthesis*; Paquette, L. A., Ed.; John Wiley & Sons: New York, 1995; Vol. 1, p 397. Also see ref 2a.

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TABLE 1. Hydrogenation of (R)-BINOL **1a**, BINOL-derived (R)-**1a–e**, and (R)-DABN **1f**^a

entry	substrate	catalyst	S/C	conditions	yield (%) of 2 ^b	ee (%) of 2 ^c	yield (%) of 3 ^b
1	BINOL (1a)	Ru/CNF-P	300	70 °C, 3 h	92	>99.9	7
2	BINOL (1a)	Ru/CNF-P	300	70 °C, 5.5 h	>95	>99.9	not detected
3	BINOL (1a)	Ru/C ^d	100	70 °C, 5.5 h	7–19	>99.9	41–57
4	BINOL (1a)	Ru/C ^e	100	70 °C, 5.5 h	11–21	>99.9	41–62
5	BINOL (1a)	Ru/CNF-P	300	50 °C, 7 h	>95 (95)	>99.9	not detected
6 ^f	BINOL (1a)	Ru/CNF-P	1390	50 °C, 48 h	>95 (99)	>99.9	not detected
7	BINOL-Me ₂ (1b)	Ru/CNF-P	300	70 °C, 5.5 h	37	—	37
8	BINOL-Me ₂ (1b)	Ru/CNF-P	300	100 °C, 5.5 h	>95 (95)	>99.9 ^g	not detected
9	BINOL-MOM ₂ (1c)	Ru/CNF-P	300	50 °C, 7 h	>95 (98)	>99.9	not detected
10	BINOL-Me (1d)	Ru/CNF-P	300	50 °C, 7 h	>95 (96)	>99.9	not detected
11	BINOL-Piv (1e)	Ru/CNF-P	300	50 °C, 7 h	>95 (92)	>99.9	not detected
12 ^h	DABN (1f)	Ru/CNF-P	150	100 °C, 24 h	83 (80)	>99.9	ⁱ

^a All reactions were carried out with 0.5 mmol of (R)-**1**, 10 mg of Ru/CNF-P (1.7 wt % Ru) in 10 mL of EtOH under H₂ (initial pressure = 40 atm).

^b Determined by ¹H NMR analysis. The yield in parentheses was the isolated yield. ^c Determined by HPLC analysis of the crude product. ^d Ru/C (5 wt %) was used. ^e Ru/C (5 wt %, dry type) was used. ^f One gram of **1a** and 15 mg of catalyst were used. ^g Determined by HPLC of **2a** after demethylation of **2b** with TMSI. ^h **1f** (0.25 mmol) was used. ⁱ Some unidentified compounds were formed as byproducts.

catalyst mole ratio of $S/C < 14$.⁹ The reaction of methoxy-methyl-protected BINOL (BINOL-MOM₂) with Raney-Ni/Al alloy afforded H₄-BINOL-MOM₂ selectively.^{7c} Higher temperature and/or addition of acids or bases accelerate the reaction, but racemization of the axial chirality is commonly observed.^{2a,7b,d} In spite of a lengthy reaction time (rt for a week) and large amounts of the catalyst ($S/C < 7$), therefore, Cram's hydrogenation procedure using PtO₂^{2a} is widely used for the production of optically pure H₈-binaphthyls.¹⁰ Thus, a hydrogenation catalyst, which can apply a variety of binaphthyl derivatives with high efficiency and no loss of optical purity, is a target to be developed. We have recently synthesized carbon nanofiber supported ruthenium nanoparticles (Ru/CNF-P) by pyrolysis of Ru₃(CO)₁₂ in the presence of platelet-type CNF (CNF-P) and found that they show high catalytic performance for the arene hydrogenation.^{11,12} Here, we report use of Ru/CNF-P as a practical solution for problematic production of H₈-binaphthyls by catalytic partial hydrogenation of 1,1'-binaphthyls.

Hydrogenation of BINOL (**1a**) was carried out in a 100 mL autoclave with **1** (0.5 mmol) and Ru/CNF-P (1.7 wt % Ru; 0.34 mol % of metal loadings; $S/C = 300$) in ethanol under hydrogen (initial pressure: $P_{\text{H}_2} = 40$ atm) (Table 1).¹³ At 70 °C, (R)-BINOL **1a** (>99.9% ee) was completely consumed in 3 h. At this stage, H₈-BINOL **2a** and H₄-BINOL **3a** were both formed

in 92 and 7% yield, respectively (entry 1). Prolonged reaction time to 5.5 h resulted in formation of **2a** as a single product in quantitative yield with >99.9% ee (entry 2). The catalytic efficiency of the Ru/CNF-P was much higher than that of two commercially available Ru/C catalysts as shown in entries 3 and 4; even with the S/C ratio of 100, conversion of **1a** was lower than 80% and a major product was H₄-BINOL **3a** (**2a/3a** = 1:6–1:2) after 5.5 h. The Ru/CNF-P-catalyzed reaction can also be performed at 50 °C, and the optically pure **2a** was obtained as a single product in 95% isolated yield after 7 h (entry 5). Ru/CNF-P does not have a reproducibility problem of heterogeneous catalysis; the desired **2a** was obtained in quantitative yields over five experiments under the conditions shown in entry 2. This is in sharp contrast to the results using commercially available Ru/C catalysts, in which conversion of **1a** was varied from 48 to 77% in three independent experiments under the conditions shown in entries 3 and 4. Application of the hydrogenation using a minimum amount of the Ru/CNF-P catalyst to a gram-scale production of **2a** was successful; the hydrogenation of **1a** (1.00 g, 3.5 mmol) using 15 mg of Ru/CNF-P (255 μg of Ru) at 50 °C for 48 h afforded the optically pure **2a** in 99% isolated yield (1.02 g). The turnover number of this reaction was calculated to be 1390 (entry 6).

The Ru/CNF-P catalyst is also useful for production of derivatives of BINOL and DABN as shown in entries 7–12. In all cases, the partial hydrogenation proceeds at 50–100 °C to afford the corresponding H₈ product in almost quantitative yield without loss of optical purity. The BINOL-derived **1c–e** were completely converted to the corresponding H₈ derivatives at 50 °C for 7 h, and optically pure **2c–e** were obtained in 92–98% isolated yields (entries 9–11). In the reaction of **1e**, the reduction of ester function was not observed under these conditions. It is noteworthy that the present procedure is useful

(9) The Pd/C-catalyzed reaction of (R)-BINOL can be performed at $S/C = 100$, but severe reaction conditions (100 °C, 80 atm) are required to obtain H₈-BINOL (99.7% ee) in high yields; see ref 7d.

(10) Optically pure H₈-BINAP is generally obtained by optical resolution of racemic H₈-bis(diphenylphosphinyl)-1,1'-binaphthyl (H₈-BINAPO), which is prepared from (±)-BINOL, followed by reduction with trichlorosilane; see ref 7a.

(11) Motoyama, Y.; Takasaki, M.; Higashi, K.; Yoon, S.-H.; Mochida, I.; Nagashima, H. *Chem. Lett.* **2006**, 35, 876.

(12) The CNFs are classified into three types: graphite layers are perpendicular (platelet: CNF-P), parallel (tubular: CNF-T), and stacked obliquely (herringbone: CNF-H). These three CNFs can be synthesized selectively in large scales; see: (a) Rodriguez, N. M. *J. Mater. Res.* **1993**, 8, 3233. (b) Tanaka, A.; Yoon, S.-H.; Mochida, I. *Carbon* **2004**, 42, 591 and 1291.

(13) The solvent strongly affected the reaction rate; the hydrogenations of BINOL in THF and dichloroethane were both sluggish, and the H₈-BINOL was obtained in <10% yields along with the formation of H₄-BINOL in ca. 20 and 50% yields, respectively.

for the production of oily binaphthyls, in which optical purity of the partially racemized product cannot be improved by recrystallization. Optically pure H₈-BINOL-MOM₂ **2c** is a typical compound of such oily binaphthyls, which can be effectively synthesized by the Ru/CNF-P-catalyzed hydrogenation in high yield (entry 9). Poor solubility of the dimethylether **1b** to ethanol retarded the reaction.¹⁴ The conversion of **1b** was 74% at 70 °C for 5.5 h, and only 37% of H₈-BINOL-Me₂ **2b** was obtained along with the formation of H₄-BINOL-Me₂ **3b** (37% yield, entry 7). Preparation of optically pure **2b** in 95% isolated yield was accomplished by the reaction at 100 °C; no byproduct was observed (entry 8).

The solubility problem was also observed in the reaction of 2,2'-diamino-1,1'-binaphthyl **1f**.¹⁴ DABN is less soluble in ethanol than BINOL-Me₂ **1b**, and the hydrogenation reaction is quite sluggish under the conditions of [**1f**] = 50 mM in EtOH: S/C = 300; below 70 °C.¹⁵ When the reaction was carried out with a lower concentration of **1f** ([**1f**] = 25 mM) and higher catalyst loading (S/C = 150) at 100 °C, (R)-DABN **1f** was successfully hydrogenated in ethanol to give **2f** in 80% isolated yield with over 99.9% ee (entry 12). Preparation of H₈-BINAP by hydrogenation of BINAP is a problem and has not yet been achieved with conventional catalysts. We also attempted the hydrogenation of BINAP in several organic solvents (S/C = 150); however, no reaction took place even at 120 °C for 48 h; BINAP was recovered quantitatively after the reaction.

Utility of the Ru/CNF catalyst in the production of H₈-binaphthyls is enhanced by its reusability. After the reaction of (R)-BINOL-MOM₂ **1c** ([**1c**] = 50 mM in EtOH, S/C = 300) was performed at 70 °C, the catalyst was recovered by filtration and subjected to a further run of hydrogenation. H₈-BINOL-MOM₂ **2c** was obtained in almost quantitative yields for the repeated uses of the catalyst (first; >99%, second; >99%, third; 96%) without loss of optical purity (>99.9% ee in all cases).

In summary, the results shown in this paper clearly demonstrate that the Ru/CNF-P-catalyzed hydrogenation of binaphthyls is useful for practical synthesis of optically pure H₈-BINOL derivatives and H₈-DABN. Although hydrogenation of BINAP has not yet been achieved, the desired H₈-BINAP is easily synthesized from H₈-DABN.¹⁶

Experimental Section

General Procedure for the Partial Hydrogenation of (R)-1,1'-Binaphthyls 1a–e. Hydrogenation of (R)-1,1'-binaphthyls **1a–e** (>99.9% ee) was performed in a 100 mL stainless autoclave fitted with a glass inner tube, in the presence of (R)-1,1'-binaphthyls **1a–e** (0.5 mmol), EtOH (10 mL), and Ru/CNF-P (1.7 wt % Ru, 10 mg; S/C = 300) at 50–100 °C for 5.5–7 h under H₂ (initial pressure = 40 atm). After the reaction mixture was cooled to ambient

temperature, the insoluble Ru/CNF-P was removed by filtration, and the filtrate was concentrated under reduced pressure. The optical purity of the produced H₈-1,1'-binaphthyls **2a–e** was determined by chiral HPLC analysis.¹⁷

(R)-2,2'-Di[(methoxymethyl)oxy]-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl (H₈-BINOL-MOM₂) (2c): Purification by silica gel chromatography (hexane/CH₂Cl₂ = 1:1); yield 98% (colorless oil); [α]_D²⁸ +48.9 (c 1.00, CHCl₃; >99.9% ee, R); IR (neat) ν 2931, 2846, 1593, 1475, 1237, 1151, 1023, 923, 803 cm⁻¹; ¹H NMR (396 MHz, CDCl₃) δ 1.60–1.78 (m, 8H), 2.10 (dt, *J* = 17.4, 6.3 Hz, 2H), 2.30 (dt, *J* = 17.4, 6.5 Hz, 2H), 2.77 (t, *J* = 6.0 Hz, 4H), 3.28 (s, 6H), 4.96 (d, *J* = 6.8 Hz, 2H), 5.02 (d, *J* = 6.8 Hz, 2H), 6.98 (d, *J* = 8.7 Hz, 2H), 7.04 (d, *J* = 8.7 Hz, 2H); ¹³C NMR (99.5 MHz, CDCl₃) δ 23.2, 23.3, 27.4, 29.5, 55.7, 94.8, 112.8, 127.2, 128.9, 131.0, 136.9, 152.2; HPLC (hexane/*i*-PrOH = 500:1), *t*_R = 15.4 min (S), 16.8 min (R); HRMS (EI) calcd for C₂₄H₃₀O₄ 382.2144, found 382.2144.

(R)-2-Hydroxy-2'-(pivaloyl)oxy-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl (H₈-BINOL-Piv) (2e): Purification by silica gel chromatography (hexane/CH₂Cl₂ = 1:1); yield 92% (colorless solid); mp 107–108 °C; [α]_D²⁶ +62.6 (c 1.00, CHCl₃; >99.9% ee, R); IR (neat) ν 3479, 2930, 2846, 1749, 1591, 1479, 1227, 1135, 809 cm⁻¹; ¹H NMR (396 MHz, CDCl₃) δ 0.95 (s, 9H), 1.59–1.81 (m, 8H), 2.02 (dt, *J* = 17.4, 5.3 Hz, 1H), 2.14 (dt, *J* = 17.4, 6.0 Hz, 1H), 2.32 (dt, *J* = 17.4, 6.3 Hz, 1H), 2.42 (dt, *J* = 17.4, 6.3 Hz, 1H), 2.63–2.77 (m, 2H), 2.77–2.88 (m, 2H), 4.73 (br s, 1H), 6.76 (d, *J* = 8.2 Hz, 1H), 6.87 (d, *J* = 8.2 Hz, 1H), 6.96 (d, *J* = 8.2 Hz, 1H), 7.16 (d, *J* = 8.2 Hz, 1H); ¹³C NMR (99.5 MHz, CDCl₃) δ 22.7, 22.9, 23.2, 23.3, 26.7, 26.9, 27.3, 29.3, 29.7, 38.7, 114.1, 119.3, 122.5, 128.1, 129.4, 129.8, 130.2, 135.85, 135.92, 138.3, 147.2, 150.8, 178.2; HPLC (hexane/*i*-PrOH = 500:1), *t*_R = 20.8 min (R), 23.0 min (S); HRMS (EI) calcd for C₂₅H₃₀O₃ 378.2195, found 378.2194.

(R)-2,2'-Diamino-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl (H₈-DABN) (2f). Hydrogenation was carried out with (R)-**1f** (0.25 mmol) and Ru/CNF-P (S/C = 150) in EtOH (10 mL) at 100 °C for 24 h under H₂ (initial pressure = 40 atm). Purification by silica gel chromatography (acetone) gave (R)-H₈-DABN **2f** in 80% yield (colorless solid): [α]_D²⁸ +70.8 (c 0.50, CHCl₃; >99.9% ee, R); ¹H NMR (396 MHz, CDCl₃) δ 1.61–1.76 (m, 8H), 2.17 (dt, *J* = 17.4, 6.5 Hz, 2H), 2.28 (dt, *J* = 17.4, 6.0 Hz, 2H), 2.71 (t, *J* = 6.0 Hz, 4H), 3.31 (br s, 4H), 6.62 (d, *J* = 8.2 Hz, 2H), 6.92 (d, *J* = 8.2 Hz, 2H); ¹³C NMR (99.5 MHz, CDCl₃) δ 23.3, 23.5, 27.1, 29.5, 113.2, 122.1, 127.7, 129.3, 136.3, 141.7; HPLC (CHIRALCEL OD-H, hexane/*i*-PrOH = 20:1), *t*_R = 24.7 min (R), 28.0 min (S). This compound was identified by spectral comparison with literature data.^{6e}

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Supporting Information Available: Spectroscopic data of **1b–e**, **2a**, **2b**, and **2d**, copies of NMR spectra of **1a–f** (¹H NMR) and **2a–f** (¹H and ¹³C NMR). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(14) In the Pd/C-catalyzed reactions, similar results and explanations were reported; see ref 7d.

(15) DABN **1f** is easily soluble in THF, but the hydrogenation of **1f** with Ru/CNF-P in THF at 100 °C did not proceed.

(16) Murdoch reported that chiral BINAP could be synthesized from optically pure DABN. Brown, K. J.; Berry, M. S.; Waterman, K. C.; Lingner, D.; Murdoch, J. R. *J. Am. Chem. Soc.* **1984**, *106*, 4717.

(17) HPLC analysis was performed on an UV/vis detector (254 nm) using Daicel CHIRALCEL OD-H (flow rate = 0.5 mL/min).